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(54) Phosphate esters of acrylated epoxides.

(57) Radiation curable monomers useful in coating compositions are prepared by reacting part of the epoxy groups of a polyepoxide resin with acrylic or methacrylic acid followed by esterifying the remaining epoxy groups with phosphoric acid.

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PHOSPHATE ESTERS OF ACRYLATED EPOXIDES

The invention relates to radiation curable compositions which are phosphoric acid esters prepared by reacting phosphoric acid with an epoxy acrylate.

Epoxy acrylates, i.e., the reaction products of acrylic acid with diepoxy compounds, are described in U.S. Patent No: 3,450,613. Resins made from bis-acrylate esters of phosphoric acid are described in U.S. Patents Nos: 3,847,846; 4,001,150 and 4,291,097. Phosphate esters of epoxy resins are described in U.S. Patents Nos: 4,164,487; 4,289,812 and 10 4,316,922.

A large number of phosphate ester compositions, including phenol bis-acrylate types and bisphenol related monoacrylates, in combination with ultraviolet sensitizers, are disclosed in U.S. Patent No: 4,259,117. Such compositions are made 15 by reacting unsaturated hydroxyl compounds with halophosphates.

Photocurable acrylic phosphate esters of epoxidised polybutadiene are described in U.S. Patent No: 4,250,007. Such compositions are made by reacting the epoxidised polybutadiene with the reaction product of polycarboxylic acids or anhydrides with hydroxyethylacrylate plus acid phosphoric dimethacrylate or acid butyl phosphate monoester.

One of the major problems in radiation curable systems has been their poor adhesion to metal due in part to the 25 low curing energy and to the resulting shrinkage of the cured film on the metal substrate. Although it is known that phosphorus containing compositions have improved adhesion to metal, it has been difficult to incorporate phosphoric acid itself into radiation curable systems.

This invention is directed to radiation curable monomers made by reacting acrylic or methacrylic acid with a polyepoxide followed by reacting the resulting acrylated epoxide with phosphoric acid. Basically, the invention involves reacting a polyepoxide having n epoxide groups per molecule, wherein n has a value of 2-4, with n-1 moles of acrylic or methacrylic acid and with 0.5 to 1 mole of phosphoric acid when

n is 2, and 1 mole of phosphoric acid when n is 3 or 4. The reaction of the phosphoric acid with the acrylated epoxy resin is conducted in the presence of a total of at least one equivalent of hydroxyl group-containing material 5 (e.g. water and/or aliphatic hydroxyl compound) per mole of phosphoric acid.

The reaction can be conducted in a reactive diluent, in amounts up to 75 weight percent diluent based on the total weight of diluent and acrylated phosphated epoxide 10 resin.

Among the surprising advantages of the invention are that it makes possible the obtaining of radiation curable systems which have excellent adhesion to metal when cured and that they are stable systems.

15 Thus the invention provides radiation curable coating compositions having good adhesion to metal.

The invention also provides compositions which may be used as radiation curable monomers.

20 The invention also provides stable phosphoric acid esters of acrylate or methacrylate esters of epoxide resins.

Other advantages of the invention will be apparent from the following description.

The polyepoxide compounds which are useful in the invention are glycidyl polyethers of aromatic or aliphatic 25 polyols having 2 to 4 epoxy groups per molecule. Such polyepoxides are well known in the art and contain terminal epoxy groups of the 1, 2 or vicinal type.

The glycidyl polyethers of aromatic polyols may be made by reacting the aromatic polyol with an epihalohydrin as 30 described in U.S. Patents Nos: 2,801,227; 2,615,007 and 2,615,008. Examples of the epihalohydrins are epichlorohydrin, epibromohydrin and epiodohydrin; epichlorohydrin is preferred. The aromatic polyols, or phenols, are exemplified by resorcinol, hydroquinone, p,p'-dihydroxydiphenyl 35 propane (or Bisphenol A as it is commonly called), p,p'-dihydroxybenzophenone, p,p'-dihydroxybiphenyl, p,p'-dihydroxydiphenyl ethane, bis(2-hydroxynaphthyl) methane, 1,5-dihydroxynaphthalene and phloroglucinol.

The glycidyl polyethers of aliphatic polyols may be made by reacting the aliphatic polyol with epihalohydrin. A detailed description of such a process can be found in U.S. Patent No: 3,033,803. Examples of useful polyols 5 include glycerine, trimethylolethane, trimethylolpropane, pentaerythritol, ethylene glycol, propylene glycol, 1,4-butanediol, hydrogenated Bisphenol A, 1,4-cyclohexane-diol, 1,3-cyclopentanediol and cyclohexanedimethanol. Additional useful polyepoxides include those based on co-10 polymers of glycidyl acrylate and methacrylate.

The polyepoxides useful in this invention generally have weights per epoxide from 100 to 1600, preferably from 175 to 550. As stated above, they have n epoxide groups per molecule, wherein n is 2 to 4.

15 The phosphoric acid used in this invention may be ortho phosphoric acid and can be utilised in its pure crystalline form or as its hydrate. Various condensed forms of phosphoric acid, pyrophosphoric acid and triphosphoric acid can also be used, provided sufficient water or aliphatic hydroxyl 20 compound is used as described hereinafter. It is preferred to use phosphoric acid in its usual commercial form which is referred to as concentrated phosphoric acid and is generally 80-90 weight percent in water.

25 The unsaturated acids which are reacted with the polyepoxide are acrylic and methacrylic acid; acrylic acid is preferred. Subject to this preference, the terms "acrylic acid" and "acrylate esters" as used in the present description are intended to include methacrylic acid and methacrylate ester as well as acrylic acid and acrylate ester.

30 The products of this invention may be prepared by first reacting sufficient acrylic acid with a polyepoxide to form an acrylate ester of the polyepoxide while leaving an epoxide group unreacted. This esterification reaction is normally carried out at a temperature of 60°C. to 150°C., preferably from 100°C. to 140°C. The reaction is normally conducted until the acid value indicates that the esterification reaction is complete, i.e., when the acid value is reduced 35 below 10. The time for the reaction will usually vary from

30 minutes to 5 hours depending on the particular reaction conditions.

In order to keep to a minimum the amount of acrylic acid polymerisation which can occur during esterification 5 it may be desirable to add 0.01-3.0% by weight, based on the total reaction mixture, of a polymerisation inhibitor. Examples of such materials include the quinones, such as hydroquinone and its monomethyl ether, the various phenols, p-tert-butylcatechol, p-methoxyphenol, 2,4- dichloro-6- 10 nitrophenol, n-propyl gallate, di-tert-butyl-p-cresol, 2,2'-methylenebis(4-methyl-6-tert-butylphenol), 1-amino-7-naphthol, p-benzoquinone, 2,6-dichloro-p-benzoquinone, 2-amino-1,4-naphthoquinone, 3-aminoanthraquinone, diphenylamine, p-nitrosodimethylaniline, α and β -naphthylamine, 15 nitrobenzene, phenothiazine, hexamethylphosphoramide, n-dodecyl mercaptan, benzenethiol, 2,2-diphenyl-1-picryl-hydrazyl (phenyl hydrazine), divinylacetylene and various antimony and copper salts. Most preferred among the inhibitors are paramethoxyphenol, hydroquinone and its mono- 20 methyl ether, phenothiazine and nitrobenzene.

In order to complete the esterification reaction at a low temperature and a reasonable reaction rate, an esterification catalyst of conventional type can be added to the reaction mixture. The esterification catalyst should be 25 added in the range of 0.1-10 percent, preferably 1-5 percent, based on the total amount of the reactants. Suitable esterification catalysts include paratoluene sulfonic acid (PTSA), methane sulfonic acid, as well as titanium esters, titanium chelates or aluminium, bismuth, barium, zinc, 30 copper, tin, chromium, calcium, antimony or cadmium alcoholates, carboxylate esters, halides or alkyl oxides and alkyl aryl ammonium halide salts.

The esterification catalyst may be removed from the reaction medium by means of a cation exchange resin. This 35 resin may be added directly to the reaction mixture and then filtered off, or the finished product may be passed through a cation exchange column. The preferred type of cation exchange resin is of the tertiary amine type. In the

alternative the insoluble salt of the reaction catalyst is formed such as by adding ammonia to a PTSA catalyst system. The reaction mixture is then filtered to remove the salted catalyst. In some cases, the esterification catalyst can 5 be retained in the product when its presence will not be deleterious to the final product properties.

Following completion of the esterification reaction between the acrylic acid and the polyepoxide as measured by a reduction to a minimum of the acid value of the. 10 reaction mixture, the temperature of the reactants may be adjusted, if necessary, and the phosphoric acid is added. in the requisite amount.

The reaction between the phosphoric acid and the epoxy acrylate is generally conducted at temperatures in the range 15 from 35°C. to 125°C., preferably from 60°C. to 90°C. The reaction may be followed by monitoring the disappearance of epoxide content of the system. Full reaction is usually attained in 30 minutes to 5 hours.

The reactant ratios for the compositions of the invention 20 may vary over narrow ranges. In carrying out the reaction, one mole of a polyepoxide having n epoxy groups per molecule is initially reacted with about n-1 moles of acrylic acid wherein n is 2-4. The resulting product is then reacted with from 0.5 to 1 mole of phosphoric acid when n is 2 and 25 with 1 mole of phosphoric acid when n is 3 or 4.

The reaction between the epoxy acrylate ester and the phosphoric acid proceeds smoothly and without gelation when a hydroxyl group containing material (normally water and/or a compound having an aliphatic hydroxyl group) is employed. 30 Such aliphatic hydroxyl containing compounds include C₁-C₂₀ alcohols, glycols, triols and glycol ethers. Examples of such compounds are methanol, ethanol, isopropanol, butanol, 2-ethylhexanol, decanol, hexadecanol, glycerine, trimethylol-ethane, trimethylolpropane, ethylene glycol, propylene glycol, 35 butylene glucol, monomethylether of ethylene glycol, mono-ethylether of ethylene glycol, monobutylether of ethylene glycol and monomethylether of diethylene glycol. The amount

of such material that is added is at least such as to provide 1 equivalent of hydroxyl for each mole of phosphoric acid that is utilised. Although there is no upper limit to the amount of hydroxyl that can be added, from a practical 5 standpoint no more than about 5 equivalents are generally utilised. The amount of water that is added includes, of course, any water which is added with the phosphoric acid. The preferred hydroxyl compound is water and the lower 10 alcohols, with water being most preferred. Mixtures of water and other hydroxyl compound can be used as long as the total equivalents of hydroxyl comply with the minimum amount. The hydroxyl material may be a polymerisable hydroxyl containing monomer; examples of such compounds include 15 hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, allyl alcohol and methallyl alcohol.

It has been found that carrying out the phosphating reaction in a reactive diluent produces products which have improved storage stability. For convenience in conducting the reaction, both stages of the reaction, i.e., the acrylic- 20 epoxy reaction and the phosphoric-epoxy reaction, can be conducted in the reactive diluent. Reactive diluents as used herein are compounds which contain one to six unsaturated groups per molecule and which can be polymerised by radiation. The reactive diluents useful in this invention 25 generally have viscosities of less than 2000 cps at 75°C. and are liquid at room temperature (25°C.), i.e., are not gaseous or crystalline. Examples of reactive diluents are acrylate and methacrylate esters of C₁-C₁₂ monohydric alcohols, vinyl esters of C₂-C₄ monocarboxylic acids, vinyl 30 aromatic monomers, vinyl heterocyclic monomers, acrylate and methacrylate esters of polyols and polyalkoxyalkyl esters of acrylic and methacrylic acid. Specific examples of such compounds include vinyl acetate, ethyl acrylate, 2-ethyl-hexylacrylate, methyl methacrylate, styrene, vinyl pyrrol- 35 idone, ethoxyethoxyethyl acrylate, hexanediol diacrylate, trimethylolpropane triacrylate, tripropylene glycol diacrylate, trimethylolethane trimethacrylate, pentaerythritol tetraacrylate and dipentaerythritol hexaacrylate. The amount

of reactive diluent used will normally vary from none at all up to 75 weight percent, preferably from 20 to 50 weight percent, based on the total weight of acrylated phosphated polyepoxide and reactive diluent.

5 For actual use as a coating composition which is radiation curable, the acrylated phosphated polyepoxides must be formulated with reactive diluents such as those described hereinbefore. The amount of reactive diluent utilised will vary depending on the viscosity desired in the coating 10 composition and on the properties desired in the cured coating. Such amounts will generally vary from 20 to 75 weight percent based on the total weight of the coating composition. If a reactive diluent is utilised during the preparation 15 of the acrylated, phosphated polyepoxide, it may form part or all of the reactive diluent in the final formulated coating composition.

The compositions of the invention are useful in radiation curable (photocurable) systems and may be cured by ultraviolet light, electron beam, curtain coaters and 20 any other type of system which utilises photons to activate the polymerisation of the unsaturated materials prepared herein. The compositions of this invention can be applied by conventional means, including brushing, spraying, dipping, curtain and roll coating techniques, and may, if desired, 25 be dried under ambient or oven conditions.

In order to render the compositions of the invention photocurable by ultraviolet light radiation, it is possible to use any of the known photosensitisers, such as benzoin, acetophenone, alkylphenone, benzophenone, tricyclic fused 30 ring, pyridal, benzoin ethers, benzil, benzil ketals and alpha-acryloxime ethers, for example as disclosed in U.S. Patent No: 4,207,155. The photosensitisers may be added to the compositions in amounts ranging from 0.1 to 15.0 percent by weight, based on the total curable system, 35 preferably from 1.0 to 5.0 percent. Although not essential, certain organic amine-type activators may be added to these compositions so as further to enhance the cure rate; these may generally be used in amounts ranging up to 500 percent

by weight, based on the photosensitiser, preferably up to 50 percent by weight. Such amines are further described in the above-mentioned U.S. Patent.

As previously stated, the compositions of the 5 invention find particular utility when used in ultraviolet curable systems to provide coatings for metal, e.g., iron, steel, copper and aluminium.

The invention accordingly provides articles bearing a cured coating based on the composition of the invention. 10 Particularly valuable products of the invention are metal articles coated with such cured coatings.

In the following Examples all parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1

15 To a suitable reactor were added 1948 parts of the diglycidyl ether of Bisphenol A having an epoxide equivalent weight of 181. Heat was applied, raising the temperature to 104°C. Acrylic acid (387 parts) was then added over a 40 minute period with the temperature being held between 20 104° and 112°C. The temperature was held at 101°C. for 1 hour and 35 minutes to complete the esterification reaction as indicated by an acid value of 0 and an epoxide equivalent weight of 489.

25 To another reactor were added 249 parts of the epoxy-acrylate prepared above. Heat was applied, raising the temperature to 49°C. Aqueous phosphoric acid (66 parts of 85% aqueous phosphoric acid plus 21 parts of additional water) was slowly added over a 30 minute period with the temperature rising to 107°C. The temperature was held at 30 107°C. for two hours, producing a product having an acid value of 144.

35 The above product was formulated into a coating composition by blending 40.25 parts of the product with 9.75 parts of ethoxyethoxyethyl acrylate and 1.5 parts of hydroxycyclohexyl phenyl ketone. Films were drawn down on steel and aluminium panels using a No: 6 Meyer Rod. The coatings were cured by ultraviolet radiation in a Fusion System Model K-523 Unit using two 300 watt/inch lamps with a line speed

of 50 ft./min. (15.24 m/min) in 2 passes.

Adhesion of the cured coatings to the substrate was determined as follows: the coatings were cross-hatched with scratch lines so as to form 100 squares. The cross-hatched area was covered with a No: 600 Scotch Brand Cellophane tape from 3M and even pressure was applied to the tape so that it would adhere evenly to the coating. The tape was then pulled from the coating and the % adhesion was determined by counting the squares which were not removed by the tape. The adhesion on the steel panels was 100%, both immediately after cure and after 24 hours. The adhesion on the aluminium panels was 98% and 100% respectively.

The phosphated acrylated product was formulated into another coating composition by blending 25 parts of the product with 17.5 parts of hydroxypropyl acrylate, 7.5 parts of trimethylolpropane triacrylate and 1.5 parts of hydroxycyclohexyl phenyl ketone. Coatings on steel panels were cured as described above. The adhesion was 100%, both initially and after 24 hours.

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EXAMPLE 2

To a suitable reactor were added 273 parts of the epoxy-acrylate described in Example 1. Heat was applied, raising the temperature to 70°C. Aqueous phosphoric acid (32.2 parts of 85% aqueous phosphoric acid plus 5 parts of additional water) was added over a 20 minute period with the temperature rising to 120°C. After the temperature had dropped to room temperature, the product had an acid value of 69 and an infinite epoxide equivalent weight.

The product (25 parts) was blended with 17.5 parts of hydroxypropyl acrylate, 7.5 parts of trimethylolpropane triacrylate and 1.5 parts of hydroxycyclohexyl phenyl ketone. Coatings were prepared and cured on steel panels using the procedure described in Example 1. The adhesion was 0% initially but was 100% after 24 hours.

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EXAMPLE 3

To a suitable reactor were added 857 parts of the diglycidyl ether of Bisphenol A having an epoxide equivalent weight of 198. The temperature was raised to 104°C., at which

point the addition of a mixture of 156 parts of acrylic acid, 1.5 parts of esterification catalyst, a chromium metal complex having a boiling point of 280°C., a viscosity of 1,325 cps at 25°C. and a specific gravity of 1.027 gm/cc, 5 and 0.7 parts of hydroquinone, was begun. The addition was completed in one hour with the temperature rising to 113°C. After holding for one hour at 113°C., the reaction was complete as indicated by an epoxide equivalent weight of 480.

10 Methanol (150 parts) was added to the reactor and the temperature was raised to 68°C. The addition of 249 parts of 85% aqueous phosphoric acid was begun and was completed in 50 minutes with the temperature being controlled between 68 and 82°C. After holding at 60°C. for 25 minutes, the 15 acid value was 144. The excess methanol was then removed by vacuum distillation. The resulting product had an acid value of 158.

20 A coating composition was prepared by blending 25 parts of the product with 17.5 parts of hydroxypropyl acrylate, 7.5 parts of trimethylolpropane triacrylate and 1.5 parts of hydroxycyclohexyl phenyl ketone. Coatings prepared on steel panels and cured as described in Example 1 had adhesion values of 100%, both initially and after 24 hours.

EXAMPLE 4

25 To a suitable reactor were added 3366 parts of the diglycidyl ether of Bisphenol A having an epoxide equivalent weight of 178. Heat was applied, raising the temperature to 104°C., at which point the addition of 680 parts of acrylic acid, 6.1 parts of chromium metal complex and 3 parts of 30 hydroquinone was begun. The addition was completed in one hour with the temperature rising to 110°C. After holding for 3 hours at 110°C., the epoxide equivalent weight was 494.

35 To another reactor were added 1780 parts of the epoxy-acrylate and 489 parts of ethoxyethoxyethyl acrylate. Heat was applied, raising the temperature to 49°C. Aqueous phosphoric acid (207 parts of 85% aqueous phosphoric acid and 32 parts of water) was added over 35 minutes with the temperature rising to 99°C. The temperature was held at

93-99°C. for one hour. The resulting product had an acid value of 62.

To 50 parts of the above product were added 1.5 parts of hydroxycyclohexyl phenyl ketone. Coatings were prepared on steel, aluminium and copper panels and were cured using the procedure described in Example 1. The adhesion on steel and aluminium was determined to be 100%, both initially and after 24 hours. The adhesion on copper was 99% initially but only 1% after 24 hours.

10 EXAMPLE 5

To a suitable reactor were added 1975 parts of the epoxy-acrylate described in Example 4, 608 parts of ethoxyethoxyethyl acrylate and 131 parts of hydroxypropyl acrylate. Heat was applied, raising the temperature to 66°C. The addition of a solution of 230 parts of 85% aqueous phosphoric acid and 131 parts of hydroxypropyl acrylate was begun and was completed in one hour and 15 minutes with the temperature rising to 82°C. The temperature rose to 93°C. and was held at this temperature for 1 hour and 20 minutes. The resulting product had an acid value of 53.6 and an epoxide equivalent weight of 49,000.

To 45 parts of the above product were added 5 parts of trimethylolpropane triacrylate and 1.5 parts of hydroxycyclohexyl phenyl ketone. Coatings were prepared on steel, aluminium and copper panels using the procedure described in Example 1. The adhesion on steel was determined to be 98% initially and 100% after 24 hours. The adhesion on aluminium was 99% initially and 60% after 24 hours. The adhesion on copper was 100% initially but 0% after 24 hours.

30 EXAMPLE 6

Using the same procedure described in the preceding Examples, 3255 parts of the diglycidyl ether of Bisphenol A having an epoxide equivalent weight of 178 were reacted with 658 parts of acrylic acid using 5.9 parts of chromium metal complex esterification catalyst and 2.7 parts of hydroquinone. The resulting product had an acid value of 0.2 and an epoxide equivalent weight of 491.

2035 parts of the epoxy-acrylate, 746 parts of ethoxyethoxyethyl acrylate, 473 parts of 85% aqueous phosphoric acid and 476 parts of hydroxypropyl acrylate were reacted, producing a product having an acid value of 108 and an epoxide equivalent weight of 32,200.

5 The resulting product (42.5 parts) was blended with 2.5 parts of ethoxyethoxyethyl acrylate, 5 parts of trimethylolpropane triacrylate and 11.5 parts of hydroxycyclohexyl phenyl ketone. Coatings were prepared on steel and aluminium 10 panels and were cured using the procedure described in Example 1. The adhesion on steel was determined to be 0% initially but 100% after 24 hours. Adhesion on aluminium was 0% initially and 95% after 24 hours.

EXAMPLE 7

15 Using the same procedure described in the preceding Examples, 1191 parts of a glycidyl polyether of Bisphenol A having an epoxide equivalent weight of 506, 319 parts of ethoxyethoxyethyl acrylate and 84.7 parts of acrylic acid were reacted to form an epoxy acrylate. This epoxy acrylate, 20 after the addition of 21.2 parts of ethoxyethoxyethyl acrylate, was reacted with 70.9 parts of 85% aqueous phosphoric acid and 11.2 parts of water. The resulting product had an acid value of 39 and an epoxide equivalent weight of 59,960.

25 The resulting product (53.3 parts) was blended with 15.6 parts of ethoxyethoxyethyl acrylate, 31.1 parts of trimethylolpropane triacrylate and 3 parts of hydroxycyclohexyl phenyl ketone. Coatings were prepared on copper, aluminium, steel, black plate and aluminium foil and were cured using the 30 procedure described in Example 1. Adhesion on copper was 100%, both initially and after 48 hours. Adhesion on aluminium was 99% initially and 100% after 48 hours. Adhesion on steel was 100%, both initially and after 48 hours. Adhesion on black plate and aluminium foil was 0% 35 in both instances.

EXAMPLE 8

Using the same procedure described in the preceding Examples, 1405 parts of a glycidyl polyether of Bisphenol A having an epoxide equivalent weight of 506, 100 parts of acrylic acid and 377.1 parts of ethoxyethoxyethyl acrylate were reacted to form an epoxy-acrylate. This epoxy-acrylate, after the addition of 56 parts of ethoxyethoxyethyl acrylate, was reacted with 193.7 parts of 85% aqueous phosphoric acid and 30.2 parts of water. The resulting product had an acid value of 61 and an epoxide equivalent weight of 75,550.

The product (62.5 parts) was blended with 7.5 parts of ethoxyethoxyethyl acrylate, 30 parts of trimethylolpropane triacrylate and 3 parts of hydroxycyclohexyl phenyl ketone. Coatings were prepared on copper, aluminium, steel, black plate and aluminium foil panels and were cured using the procedure described in Example 1. Adhesion on copper was determined to be 0% initially but 90% after 48 hours. On aluminium adhesion was 0% initially and 100% after 48 hours. On steel, the adhesion was 100%, both initially and after 48 hours. On black plate, it was 0% initially and 80% after 48 hours. On aluminium foil, it was 0%, both initially and after 48 hours.

EXAMPLE 9

To a suitable reactor were added 625 parts of the diglycidyl ether of Bisphenol A having an epoxide equivalent weight of 191. Heat was applied, raising the temperature to 121°C. A monomer-catalyst solution of 1072 parts of butyl acrylate, 380 parts of vinyl acetate, 457 parts of glycidyl methacrylate, 55 parts of azobisisobutyronitrile and 53.7 parts of n-octyl mercaptan was added over a 3 hour period with the temperature varying between 121°C. and 129°C. Heating up to 150°C. was continued for 1 hour. The temperature was adjusted to 104°C. and a solution of 350 parts of acrylic acid, 7.5 parts of chromium metal complex esterification catalyst and 2.8 parts of hydroquinone was added over 1 hour with the temperature being held at 110°-127°C. After the completion of the addition, heating at 107°C. was continued for 50 minutes. The acid value was

0.01 and the epoxide equivalent weight was 2588.

The temperature was dropped to 58°C and aqueous phosphoric acid (128.8 parts of 85% aqueous phosphoric acid and 40.3 parts of water) was added over a period of 1 hour and 5 minutes with the temperature being held at 58°C. After holding for an additional hour at this temperature, the product had an acid value of 40 and an epoxide equivalent weight of 22,500.

Coatings prepared from this composition were cured by ultraviolet radiation using the procedures described in the preceding Examples.

CLAIMS

1. A process for preparing a radiation curable material which comprises reacting 1 mole of a polyepoxide having n epoxide groups per molecule, wherein n has a value of 2 to 4, with about n-1 moles of acrylic acid or methacrylic acid, followed by reaction of the resulting product with 0.5 to 1 mole of phosphoric acid when n is 2 and 1 mole of phosphoric acid when n is 3 or 4, in the presence of at least 1 equivalent of a hydroxyl group-containing material per mole of phosphoric acid.
2. The process of claim 1 wherein the first acid is acrylic acid.
3. The process of claim 1 or 2 wherein the hydroxyl-containing material is or comprises water.
4. The process of any of claims 1 - 3 wherein the hydroxyl group-containing material is an aliphatic hydroxyl group-containing compound.
5. The process of claim 4 wherein the aliphatic hydroxyl group-containing compound is a C_1-C_{20} alcohol.
6. The process of any of claims 1 - 5 wherein the polyepoxide is a polyglycidyl ether of a dihydric phenol.
7. The process of any of claims 1 - 5 wherein n is 2.
8. The process of any of claims 1 - 7 wherein at least the phosphoric acid reaction is conducted in the presence of a reactive diluent, wherein said reactive diluent contains 1 to about six unsaturated groups per molecule.
9. The process of claim 8 wherein the reactive diluent is present in an amount up to 75 weight percent based on total weight of acrylated phosphated polyepoxide and reactive diluent.
10. The process of claim 9 wherein the reactive diluent is present in the amount of 20 to 50 weight percent.

11. A material prepared by the process of any of claims 1 - 10 in the form of a curable coating composition containing 20 to 75 weight percent of reactive diluent based on total weight of the curable coating composition.
12. Articles coated with a cured coating of the composition of claim 11.
13. Metal articles coated with an adhesive coating of the composition of claim 11.